approaches, at pH 13, a limiting value nearly half that in acid solution. The quenching process is obviously different from that present for the complexes $Cr(NH_3)_6^{3+}$ and $Cr(en)_3^{3+}$, where total phosphorescence quenching was observed at pH values ≥ 11. For the latter compounds we have suggested[8] involvement of an amine–hydrogen deprotonation step, a mechanism unavailable to $Cr(phen)_3^{3+}$. The pH profile for phosphorescence intensity (Figure 2) is suggestive of hydroxide ion addition to either ground- or excited-state $Cr(phen)_3^{3+}$, resulting in the equilibrium formation of a Meisenheimer-type complex.[9] Since phosphorescence occurs between levels predominantly metal in character, the absence of a spectral shift in the basic emission spectrum is consistent with this model of peripheral hydroxide attack on an aromatic ring.

One way to account for an increase in ϕ_{rac}, on a decrease in phosphorescence, and a continuing small fraction of non-quenchable reaction would be to suggest that a *reaction* from the doublet has been observed; with our results, this conclusion cannot be regarded as firm. However, Moggi, Balzani, and Bolletta[10] have very recently developed a strong case for bimolecular reaction between OH^- and the doublet of $Cr(bpy)_3^{3+}$.

Racemization Mechanism in Acid or Neutral Solution. Although the ultimate product of $(+)_{589}$-$Cr(phen)_3^{3+}$ photolysis is $(\pm)$-$Cr(phen)_2(H_2O)_2^{3+}$, loss of optical activity proceeds at a rate well in excess of photoaquation for pH ≤ 7. Thus, after 2.5 half-lives of racemization at 350 nm in the presence of Fe(II), no evidence for free phenanthroline was obtained. Rotation loss is therefore attributed to direct racemization, $(+)_{589}$-$Cr(phen)_3^{3+} \rightarrow (\pm)$-$Cr(phen)_3^{3+}$.

Direct racemization could proceed by either intermolecular or intramolecular mechanisms.[11] Of these pathways, an intermolecular mechanism is considered the less probable. Although the lack of a ferroin color test is by no means unequivocal, it does require that the steady-state concentration of free phenanthroline be exceedingly small if an intermolecular scheme is operative. A variety of twist and one-ended dissociation mechanisms of intramolecular racemization have been suggested for tris-bidentate complexes.[12] Basolo and others[13,14] have pointed out that a one-ended dissociation pathway for phenanthroline chelates is also unlikely. Owing to the rigid nature of the ligand, any "half-bonded" structure should normally be expected to undergo ring closure with retention of configuration. However, it is noteworthy that after 2.5 half-lives for racemization, a small decrease ($\sim 8\%$) in phosphorescence intensity is observed. Since this change cannot be attributed to photoaquation or to a twist pathway, it is possible that some racemization proceeds through the intermediacy of the ring-opened species cis-$Cr(phen)_2phen$-$(H_2O)^{3+}$.

Registry No. $(+)_{589}$-$Cr(phen)_3^{3+}$, 41587-82-0; SCN^-, 302-04-5; I^-, 20461-54-5; O_2, 7782-44-7; OH^-, 14280-30-9.

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(6) Assuming an energy maximum for fluorescence similar to that reported for $Cr(bpy)_3^{3+}$ (bpy = 2,2'-bipyridine),[4] we estimate a $^4T_{2g}$–^2E_g zero-point energy gap of ≥ 10 kcal mol^{-1} for $Cr(phen)_3^{3+}$ by dividing the Stokes shift by 2.
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Convenient Preparations of 1,2,3,4,5-Pentamethylcyclopentadiene and 1-Ethyl-2,3,4,5-tetramethylcyclopentadiene
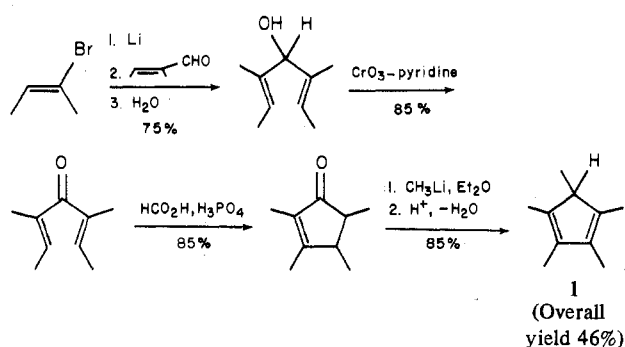
David Feitler and George M. Whitesides*

Pentamethylcyclopentadienyl (Me_5Cp) anion is a useful cyclopentadienyl congener in transition metal chemistry.[1,2] Investigation of Me_5Cp–metal compounds has been hindered by the inaccessibility of pentamethylcyclopentadiene (1).[1,3] The most commonly used synthesis[3] (Scheme I) is inconvenient and expensive and the optimal experimental conditions[4] have not been widely disseminated. Although specialized reactions yield Me_5CpM derivatives,[5,6] no general, large-scale preparation of pentamethyl- or other polyalkylated cyclopentadiene derivatives has been available.
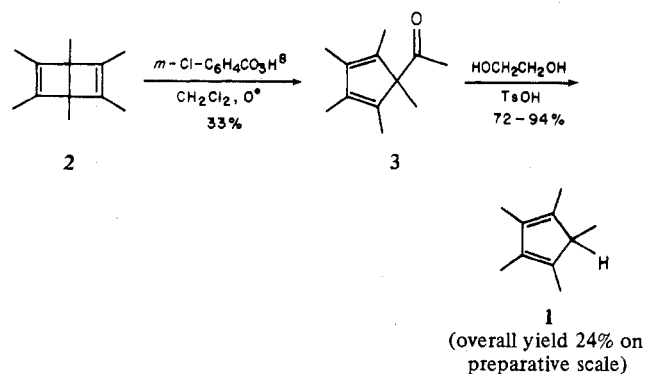
Burger et al. recently reported two short syntheses of Me_5Cp which are practical for large-scale preparations (Scheme II).[7] The starting material in the first of these syntheses, hexamethyl(Dewar benzene) (2) is expensive and sensitive. We have repeated the cleavage of 3 to 1 following the reported method[7] on a preparative scale and found it to be an efficient and convenient method. The second procedure provides an inexpensive route to tetramethylcyclopentenone (4), an intermediate also used in the previous synthesis.[3] We have not reproduced the second route.

Here we describe a fourth route to 1 and a particularly convenient preparation of 1-ethyl-2,3,4,5-tetramethylcyclopentadiene (9) (Scheme III). This synthesis of 1 is based on the work of Conia[9] and Eaton.[10] 2-Butyl tiglate (6) is prepared either by acid-catalyzed esterification of tiglic acid (5) or by allowing tigloyl chloride to react with 2-butanol. Compound 6 is cyclized and dehydrated to tetramethylcyclopentenone (4) using 1:10 solution of P_2O_5 in methanesulfonic acid.[10] This medium proved superior to PPA for this cyclization (see the Experimental Section). Addition of methyllithium to 4 and dehydration of the resulting alcohol to 1 follow previous syntheses.[3,7] The synthesis of 9 begins with dimerization of 3-pentanone to 4,5-dimethyloctane-3,6-dione (7) by refluxing with lead dioxide.[11] This procedure is both more convenient and safer than that requiring acetyl peroxide,[12] and it is not necessary to isolate 7. After simple distillation of excess 3-pentanone, a base-catalyzed internal aldol condensation converts 7 to 8; addition of methyllithium and dehydration affords 9. Compound 9 was characterized by NMR spectroscopy and by conversion to ethyltetramethylcyclopentadienyl ($EtMe_4Cp$) derivatives of titanium and iron (($EtMe_4Cp)_2TiCl_2$ and ($EtMe_4Cp)_2Fe$).
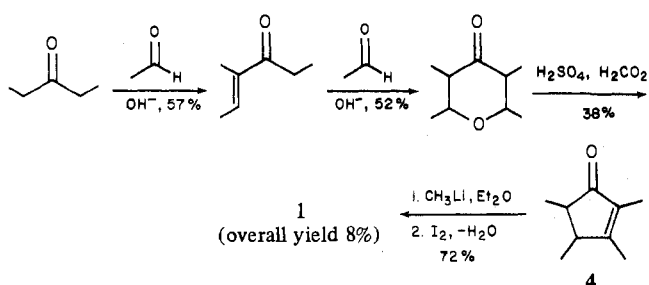
The relative merits of these new methods for preparation of pentaalkylcyclopentadienes are based on cost and convenience. The most convenient of these four preparations for large-scale work is that leading from 3-pentanone to 9 (method

Notes

Scheme I. Synthesis of Pentamethylcyclopentadiene (1) Based on Butenyllithium (Method 1)[3,4]

1
(Overall
yield 46%)

Scheme II. Syntheses of Pentamethylcyclopentadiene Reported by Burger et al.[7]

Method 2

1
(overall yield 24% on
preparative scale)

Method 3

1
(overall yield 8%)

4

Scheme III. New Syntheses of Pentamethylcyclopentadiene (3) and Ethyltetramethylpentadiene (9)

Method 4

1
(overall yield 34%)
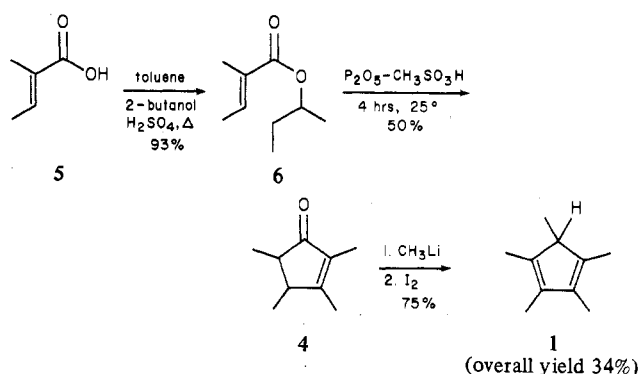
Method 5

(mixture of isomers)
9
(overall yield 28%)

5). Starting materials are inexpensive and the procedure is easily carried out on a scale that yields 100–200 g of **9**. Although organometallic derivatives of EtMe₄Cp lack the aesthetic symmetry afforded by Me₅Cp, they have the compensating advantage of higher solubility ((EtMe₄Cp)₂TiCl₂ is soluble in both toluene and hexane while (Me₅Cp)₂TiCl₂ is insoluble in these solvents) and lower melting points (Cp₂Fe, 171°; (Me₅Cp)₂Fe, 291–295°; (EtMe₄Cp)₂Fe, 145°; Cp₂TiCl₂, 289–291°; (Me₅Cp)₂TiCl₂, 273°; (EtMe₄Cp)₂TiCl₂, 200–201°).

Hexamethyl(Dewar benzene) (**1**) is not an inherently expensive material and reduction of its current price would unquestionably render method 2 the best route to **1**. Both methods 2 and 4 produce **1** in comparable yields (24% and 34%, respectively), but method 4 has the disadvantage that an additional step is required. Tiglic acid is, however, less expensive than hexamethyl(Dewar benzene). Method 1 is clearly less convenient as a procedure to **1** than are methods 2 and 4. We have attempted to prepare 2-butyl tiglate (**6**) directly from 2-bromo-2-butene, carbon monoxide, and 2-butanol following the procedure of Heck et al.[13] but have not been able to produce more than trace amounts.
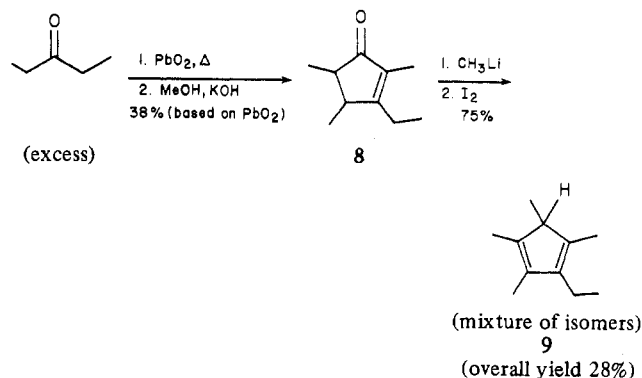
All of the methods discussed have particular applications as large-scale preparatory methods for pentaalkylated cyclopentadienes. Symmetrical cyclopentadienes are available

from the appropriate starting materials in methods 3–5. Varying degrees of substitution may be induced in method 3 by variations of aldehyde and/or ketone used and in method 4 by use of analogues of tiglic acid and 2-butanol. Method 5 generates a product of lower symmetry than Me₅Cp. Of course, substituents may be varied in derivatives made by methods 3–5 by the addition of alkyllithium compounds other than methyllithium to the tetraalkylcyclopentenone, although steric hindrance may become a problem with the more highly substituted cyclopentenones.

We note finally that the procedure for preparation of metallocenes using lithium cyclopentadienide given in the Experimental Section is superior to those previously reported and is applicable to pentamethylcyclopentadiene as well.[14]

Experimental Section

The following chemicals were obtained from the indicated suppliers: tiglic acid, 3-pentanone, thionyl chloride, methanesulfonic acid (practical grade) (Eastman); P₂O₅ (Mallinckrodt); 2-butanol (Aldrich); methyllithium (in Et₂O) and titanium trichloride (Alfa); lead dioxide (Fischer); polyphosphoric acid (MCB). Ir spectra were taken using a PE Model 567 spectrophotometer, and NMR spectra using a Varian T-60 spectrometer. Melting points, boiling points, and pressures are uncorrected. Elemental analyses were performed by Robertson Laboratory, Florham Park, N.J. Both Me₅CpH and EtMe₄CpH should be stored at −10°.

2-Butyl Tiglate (6). Method A. A mixture of 400 ml of 2-butanol, 400 ml of toluene, 46 g (0.46 mol) of tiglic acid, and 10 ml of concentrated H₂SO₄ was refluxed for 18 hr while separating water in a Dean-Stark trap. The mixture was cooled, extracted once with 100 ml of water, dried (Na₂SO₄), and concentrated. The resulting oil was distilled through a 30-cm heated Holzmann column giving 65.1 g (93%) of 2-butyl tiglate having bp 66° (8 Torr), lit.[15] bp 87.5° (27 Torr). NMR (CDCl₃): δ (TMS) 6.82 (m, 1), 4.53 (sextuplet, 1, $J \approx 6$ Hz), 1.85 (s, broad, 6), 1.52 (q, 2, $J \approx 6$ Hz), 0.90 (d, 3, $J \approx 6$ Hz), 0.73 (t, 3, $J \approx 6$ Hz).

Method B.[16] Tiglic acid (25 g, 0.25 mol) and thionyl chloride (37 g, 0.28 mol) were heated for 2 hr on a steam bath. Excess thionyl chloride was removed by evaporation at reduced pressure, 2-butanol

(25 ml) was added, and the mixture was heated until the evolution of HCl ceased. The resulting oil was distilled to give 35 g (89%) of **6**.

2,3,4,5-Tetramethylcyclopent-2-enone (4). Method A. 2-Butyl tiglate (15.6 g, 0.1 mol) was magnetically stirred with 150 g of a 1:10 P_2O_5-methanesulfonic acid mixture (prepared by mechanically stirring 1 part of P_2O_5 into 10 parts of practical (95%) methanesulfonic acid)[10] for 4 hr at room temperature. The deep red mixture was added dropwise over 2 hr to 350 ml of water, and aqueous material was extracted with 300 ml of pentane. The pentane solution was washed once with 100 ml of saturated aqueous $NaHCO_3$ solution and once with 100 ml of saturated aqueous NaCl solution, dried (Na_2SO_4), and concentrated. Distillation gave 7.6 g of **4** as a mixture of isomers having bp 100° (30 Torr), lit.[3] bp 59.8° (3.3 Torr), which was 92% pure by glpc (50% yield).

Method B. A 2-l. flask fitted with a reflux condenser, a mechanical stirrer, and a thermometer was charged with 600 g of PPA and 90 g (0.19 mol) of 2-butyl tiglate. The mixture was heated to 90° for 10 min[17] and then quenched by the careful addition of ice water. Its final color was deep red. The hydrolyzed reaction mixture was extracted with pentane (1 l.) and the pentane solution extracted with 250 ml of 1 *N* aqueous NaOH solution. From the aqueous base, 9.6 g of impure tiglic acid was recovered by acidification, extraction, and crystallization. The pentane solution was further extracted with water, saturated aqueous $NaHCO_3$ solution, and saturated aqueous NaCl solution. Drying (Na_2SO_4), concentration, and distillation gave 26 g of material having bp 51–58° (6 Torr) which was 81% **4** by GLC (26%). This material was contaminated by two higher boiling fractions. It was not necessary to remove these contaminants.

1,2,3,4,5-Pentamethylcyclopentadiene (1). To a solution of 26 g (0.15 mol) of crude **4** (from the above preparation) in 300 ml of ether maintained at 0° in an ice bath and magnetically stirred under nitrogen was added 120 ml of 2.2 *M* methyllithium (0.28 mol) using a syringe. The mixture was stirred overnight. Excess methyllithium was destroyed by cautious addition of 30 ml of 2-propanol. The solution was poured into water and extracted with ether, and the combined organic layers were treated with a few crystals (ca. 100 mg) of iodine.[18] Water was allowed to separate for 2 hr. The resulting solution was washed with 0.1 *M* $Na_2S_2O_4$ solution (400 ml) and saturated aqueous NaCl solution (150 ml) and dried (Na_2SO_4). Concentration and distillation gave 15.6 g (75%) of **1** (bp 51° (7 Torr), lit.[3] bp 58.3° (13.5 Torr)). NMR (CDCl₃): δ 2.5 (m, 1), 1.83 (s, broad, 15).

Pentamethylcyclopentadiene (Method 2).[7] A mixture of 20 g (0.112 mol) of 1-acetyl-1,2,3,4,5-pentamethylcyclopentadiene,[6] 20 ml (0.36 mol) of ethylene glycol, and 0.3 g of *p*-toluenesulfonic acid hydrate was refluxed overnight while separating water in a Dean-Stark trap. The mixture was cooled, extracted once with 100 ml of water, twice with 100-ml portions of saturated aqueous $NaHCO_3$ solution, and once with saturated aqueous NaCl solution, and dried (Na_2SO_4). Concentration at reduced pressure and distillation gave 11 g (72%) of **3**, bp 47° (5 Torr).

3-Ethyl-2,4,5-trimethylcyclopent-2-en-1-one. A mixture of 1 kg (2.1 mol) of lead dioxide and 1.7 l. of 3-pentanone was mechanically stirred at reflux overnight. Yellow lead oxide was removed by filtration and excess 3-pentanone and water were removed by distillation. The residue was taken up in 1.5 l. of methanol and stirred overnight with 5 g of KOH. The base was neutralized with 7.5 ml of concentrated HCl, the methanol evaporated at reduced pressure, and the residue extracted with equal volumes of water, 1 *N* aqueous NaOH solution, saturated aqueous $NaHCO_3$ solution, and saturated aqueous NaCl solution and dried (Na_2SO_4). Distillation gave 87 g (38%) of **8**, as a mixture of isomers, bp 81–84° (6 Torr). Ir (CCl₄): 1694 (C=O), 1642 (C=C) cm⁻¹. This compound was not characterized further but was used directly.

Ethyltetramethylcyclopentadiene (9). Cyclopentenone **8** was dried immediately before use by passage through 40 g of crude Woelm alumina (activity I). A 2-l. round-bottomed flask equipped for magnetic stirring and fitted with a precalibrated addition funnel capped with a No-Air stopper was flame-dried and purged with dry nitrogen. After cooling, 174 g (1.15 mol) of freshly dried **8** and 450 ml of dry ether were added directly to the flask via cannula and then 735 ml (1.25 mol) of 1.7 *M* ethereal methyllithium was added to the addition funnel, again by cannula. The flask was immersed in an ice bath and the methyllithium added slowly over 2 hr. The mixture was allowed to warm to room temperature and stir overnight. Excess methyllithium was destroyed by the cautious addition of 2-propanol(20 ml) and the

ethereal solution was extracted with water. To the ether layer was added 0.5 g of iodine. Over 0.5 hr 18 ml of water separated. The etheral layer was extracted twice with 100-ml portions of 0.1 *M* $Na_2S_2O_4$ solution and twice with 100-ml portions of saturated aqueous NaCl solution, dried (Na_2SO_4), and concentrated to give 164.5 g of light yellow oil (95% crude yield). Distillation gave 130 g (75%) of **9** (EtMe₄CpH) bp 59–61° (5 Torr), as a mixture of isomers. This material was not further characterized but used directly in the following reactions.[19]

(EtMe₄Cp)₂Fe. Ferrous chloride was prepared by stirring at reflux 0.97 g (6 mmol) of FeCl₃, 0.169 g (3 mmol) of iron powder (electrolytically reduced, 300 mesh), and 20 ml of THF (distilled from benzophenone ketyl) for 5 hr under argon. A 0.052 *M* slurry of EtMe₄CpLi was prepared by the addition of 150 ml of 1.70 *M* methyllithium to a solution of 13.0 g of EtMe₄CpH in 20 ml of dry Et₂O, evaporation of ether, and replacement with THF. An aliquot of this slurry (42 ml) was added to the ferrous chloride preparation at room temperature via syringe. The reaction was stirred overnight at reflux, quenched with water, and extracted with 200 ml of CHCl₃. The organic layer was washed with saturated aqueous NaCl solution, dried (Na_2SO_4), and concentrated to give 1.7 g (53% crude) of (EtMe₄Cp)₂Fe. Three recrystallization from CHCl₃–MeOH gave clear yellow crystals (0.9 g), mp 145° (sealed tube). NMR (CDCl₃): δ 2.16 (q, 2, *J* = 7.6 Hz), 1.70 (s, 24), 0.9 (t, 6, *J* = 7.6 Hz). Mass spectrum (70 eV): M⁺ – 1, 353. Ir spectrum (KBr, cm⁻¹): 2960, 2900, 2860, 1470, 1450, 1420, 1375, 1025. Anal. Calcd for $C_{22}H_{34}Fe$: C, 74.57; H, 9.67. Found: C, 74.72; H, 9.73.

(EtMe₄Cp)₂TiCl₂. Titanium trichloride (15.4 g, 100 mmol) was transferred in a drybox into a dry, 1-l. three-necked flask fitted with No-Air stoppers and equipped for magnetic stirring. The flask was removed from the drybox, 175 ml of dry THF was added via a syringe, the flask was flushed with argon, and one stopper was replaced with a reflux condenser. A suspension of EtMe₄CpLi in THF prepared as described above (375 ml, 300 mmol) was added via syringe at room temperature and the mixture was refluxed overnight. After cooling of the mixture to 0° in an ice bath, 500 ml of 12 *N* HCl was added, the resulting dark red solution was extracted with 1 l. of CHCl₃, and the organic phase was dried (Na_2SO_4). Evaporation gave 25.5 g (61%) of (EtMe₄Cp)₂TiCl₂. Recrystallization from CHCl₃–MeOH gave lustrous purple-brown crystals, mp 200.5–201°. NMR (CDCl₃): δ 2.50 (q, 4, *J* = 7.6 Hz), 2.03 (s, 24), 0.95 (t, 6, *J* = 7.6 Hz). Mass spectrum (70 eV): M⁺, 416. Ir (KBr, cm⁻¹): 2960, 2900, 1450, 1430, 1390, 1380, 1365, 1048, 1020. Anal. Calcd for $C_{22}H_{34}Cl_2Ti$: C, 63.32; H, 8.21; Cl, 16.99. Found: C, 63.25; H, 8.48; Cl, 17.25.

Registry No. Tiglic acid, 80-59-1; 2-butanol, 78-92-2; 2-butyl tiglate, 28127-58-4; 2,3,4,5-tetramethylcyclopent-2-enone, 54458-61-6; 1,2,3,4,5-pentamethylcyclopentadiene, 4045-44-7; methyllithium, 917-54-4; 1-acetyl-1,2,3,4,5-pentamethylcyclopentadiene, 15971-76-3; 3-pentanone, 96-22-0; 3-ethyl-2,4,5-trimethylcyclopent-2-en-1-one, 57459-40-2; ethyltetramethylcyclopentadiene, 57459-41-3; (EtMe₄Cp)₂Fe, 57473-98-0; (EtMe₄Cp)₂TiCl₂, 57473-99-1.

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(17) Yields and purities are highly susceptible to variations in temperature and stirring efficiency. The reaction is exothermic above 80°, and inefficient stirring in large-scale preparations can lead to very high internal temperatures with reduction in yield and concomitant loss of purity.
(18) A few drops of 6 N HCl will also suffice and may result in a cleaner product.[14]
(19) The material is obtained as a mixture of isomers, and extensive purification does not simplify the spectrum. Prominant NMR resonances (CDCl₃) are observed at δ 2.45 (q, 2, J = 7 Hz), 1.80 (s, 12, broad), 0.98 (t, 3, J = 7 Hz).

Contribution from the Department of Chemistry,
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Kinetics of Isomerization of *trans*-Dicarbonyl Phosphine Complexes of Molybdenum(0) and Tungsten(0)

Clive M. Elson

Recently, electrochemical and x-ray photoelectron spectroscopic studies have been performed to determine the electron distribution within dinitrogen complexes of rhenium,[1,2] molybdenum, and tungsten[3] and their analogues. During the work, preparations of both the cis and trans isomers of dicarbonylbis(1,2-diphenylphosphinoethane)molybdenum(0 and I) and -tungsten(0 and I) were attempted. It was found, however, that only one isomer was stable in a given metal oxidation state, as previously reported.[4-8] The isomerization of *trans*-[M(CO)₂dpe₂] (M = Mo and W, dpe = Ph₂PCH₂CH₂PPh₂) has now been monitored electrochemically and the kinetics of the reaction are described here.

The starting materials, *cis*-[M(CO)₂dpe₂] (M = Mo and W), were prepared by published procedures. The dicarbonyl complexes displayed one-electron irreversible oxidation waves (E_{pa} = +0.035 and +0.067 V for M = Mo and W, respectively, vs SCE) when examined by cyclic voltammetry at a vitreous carbon electrode in a CH₂Cl₂–MeOH (10:1 v/v)–0.1 N Et₄NBF₄ electrolyte. The irreversibility of the oxidation process is due to the very rapid conversion of *cis*-[M(CO)₂dpe₂]⁺ (M = Mo and W) to the trans form.[8] Bulk-scale controlled potential oxidations of the cis metal(0) dicarbonyls at +0.2 V on a platinum electrode produced *trans*-[M(CO)₂dpe₂]BF₄. The metal(I) salts were characterized by elemental analysis (e.g., calcd for [W(CO)₂dpe₂]BF₄: C, 57.2; H, 4.99. Found: C, 57.7, H, 4.27), infrared [single CO stretching frequency at 1860 cm⁻¹ (Nujol) for M = Mo and at 1850 cm⁻¹ (Nujol) for M = W], conductivity (Λ_M = 32.5 ohm⁻¹/cm² for *trans*-[Mo(CO)₂dpe₂]BF₄ in 1,2-dichloroethane), and molecular weight measurements (e.g., *trans*-[Mo(CO)₂dpe₂]BF₄, expected 518 for a 1:1 electrolyte, found 499).

The metal(I) complexes were reducible at -0.363 and -0.350 V for M = Mo and W, respectively. At high scan rates, the reduction was consistent with a reversible, one-electron, diffusion-controlled, charge transfer.[9,10] However, when the voltage sweep rate was decreased or a multicycle voltammogram was run, a second oxidation wave appeared near 0.0 V (Figure 1). As time elapsed, the height of the second wave increased at the expense of the oxidation wave at -0.28 V. This
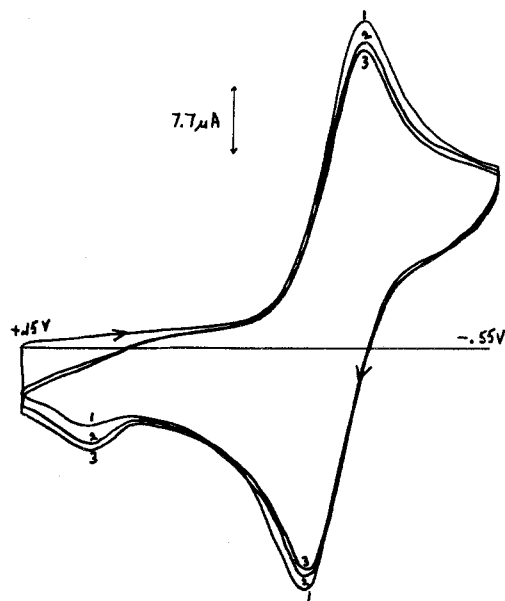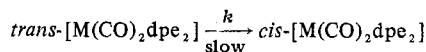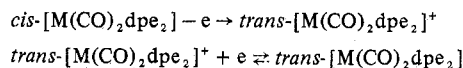

Figure 1. Multicycle voltammogram of *trans*-[Mo(CO)₂dpe₂]-BF₄ at a vitreous carbon electrode in CH₂Cl₂–MeOH–0.1 N Et₄NBF₄ at ν = 0.09V sec⁻¹.

Table I. Rate Constants for Isomerization of *trans*-[M(CO)₂dpe₂]

trans-[M-(CO)₂dpe₂]	Electrolyte	Temp, °C	k, sec⁻¹ × 10
M = W	A[a]	20	0.9 ± 0.2
Mo	A	20	0.6 ± 0.1
Mo	A + 5-fold excess dpe	20	0.7 ± 0.2
Mo	A + 15-fold excess dpe	20	0.5 ± 0.1
Mo	Thf-MeOH-LiCl (0.1 N)	20	0.3 ± 0.1
Mo	B[b]	11.4	0.36 ± 0.08
Mo	B	11.5	0.34 ± 0.08
Mo	B	11.7	0.42 ± 0.09
Mo	B	19.7	0.70 ± 0.17
Mo	B	28.0	1.4 ± 0.3
Mo	B	27.9	1.3 ± 0.3
Mo	B	38.4	3.2 ± 0.8
Mo	B	38.5	3.1 ± 0.8

[a] A is CH₂Cl₂–MeOH (10:1 v/v)–Et₄NBF₄ (0.1 N).   [b] B is CH₂-Cl–MeOH (10:1 v/v)–Et₄NBr (0.1 N).

suggested that the trans metal(0) complexes, generated by reduction, slowly isomerized to the cis configuration. Controlled potential reductions at -0.4 V of *trans*-[M(CO)₂dpe₂]⁺ (M = Mo and W) produced cis metal (0) dicarbonyls in 100% yields confirming that a geometric rearrangement occurred. An overall reaction scheme can be written:

cis-[M(CO)₂dpe₂] − e → *trans*-[M(CO)₂dpe₂]⁺

trans-[M(CO)₂dpe₂]⁺ + e ⇌ *trans*-[M(CO)₂dpe₂]

$$trans\text{-}[M(CO)_2dpe_2] \xrightarrow[\text{slow}]{k} cis\text{-}[M(CO)_2dpe_2]$$

where M = Mo and W.

The rate of isomerization (k) was studied by the method of Schwarz and Shain[11] assuming that the reaction was first or pseudo-first order. Double potential step chronoamperograms at -0.15 and -0.5 V were recorded and the ratio of the reduction current of *trans*-[M(CO)₂dpe₂]⁺ to the oxidation current of *trans*-[M(CO)₂dpe₂] was determined at various times subsequent to the application of the potential. The pulse times varied from 1 to 10 sec and six determinations of k were made from each chronoamperogram and an average was taken.

The isomerization reaction was studied in a variety of electrolytes and at various temperatures (Table I). An Arrhenius plot for the rearrangement of *trans*-[Mo(CO)₂dpe₂] was linear (correlation coefficient = 0.997) and yielded an